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(54) THICK-FILM RESISTANCE PASTE AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thick-film resistance paste, having high EDS characteristic (high withstand voltage pulse characteristic) and which does not contain such harmful substance as Pd, Cd, Ni, etc., for obtaining a ceramic circuit board having superior performance.

SOLUTION: A film resistance paste is prepared by adding an organic vehicle, a solvent, and a dispersant to a mixture prepared by mixing raw material powder composed of glass powder and conductive material powder with the organic vehicle. The mixture is prepared for satisfying the relation, $5.5A \leq B \leq 10.0A$ (where A represents the mean specific surface area (Am^2/g) of the raw material powder, when the minor-axis diameter of the powder is less than or equal to $5\mu\text{m}$ and the volumetric ratio (%) of the vehicle to the raw material powder is B). At the manufacturing of the paste, the raw material powder is dispersed in the organic vehicle by forcibly passing the raw material mixture through a clearances of less than or equal to $5\mu\text{m}$ in width.

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CLAIMS

[Claim(s)]

[Claim 1] In the thick-film resistive paste which makes the mixture which comes to mix the raw material powder which consists of glass powder and powder of conductive material with an organic vehicle come to add an organic vehicle, a solvent, and a dispersant further Thick-film resistive paste characterized by using the mixture which has the relation of $5.5 A \leq B \leq 10.0A$ when the minor-axis particle size of this raw material powder makes B % the volume rate of as opposed to this raw material powder of $A m^2/g$ and this organic vehicle for average specific surface area, by 5 micrometers or less.

[Claim 2] Thick-film resistive paste according to claim 1 which is that in which the above-mentioned raw material powder ingredient does not contain Pb, Cd, and nickel.

[Claim 3] Thick-film resistive paste according to claim 1 whose above-mentioned conductive material is RuO₂.

[Claim 4] In the process which passes a clearance 5 micrometers or less for the mixture which consists of a powder ingredient and an organic vehicle compulsorily, and makes an organic vehicle distribute a raw material powder ingredient The manufacture approach of the thick-film resistive paste characterized by consisting of mixture which has the relation of $5.5 A \leq B \leq 10.0A$, and nothing and the process which adds and kneads an organic vehicle, a solvent, and a dispersant further when the volume rate of $A m^2/g$ and an organic vehicle is made into B % for the average specific surface area of raw material powder.

[Claim 5] The manufacture approach of the thick-film resistive paste according to claim 4 which is that in which the above-mentioned raw material powder ingredient does not contain Pb, Cd, and nickel.

[Claim 6] The manufacture approach of thick-film resistive paste according to claim 4 that the above-mentioned conductive material is RuO₂.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thick-film resistive paste and its manufacture approach for [which has an external resistance object] the ceramic circuit boards.

[0002]

[Description of the Prior Art] In the ceramic circuit board used for an integrated circuit, the circuit which consists of a conductor pattern, an external resistance object, etc. on the surface of [other than the built-in resistor prepared between the layers of a multilayered circuit board] a ceramic substrate is formed, and it is contributing to advanced features of the ceramic circuit board, and low cost-ization.

[0003] When forming a thick film resistor in a ceramic substrate front face, what added conductive material to glass powder and was made into the shape of a paste with the organic vehicle is printed and sintered on a substrate front face, and it considers as a resistor. At this time, it prints so that a resistor may be covered with a textile-glass-yarn ingredient for the purpose of protection of a resistor, or improvement in weatherability, and carrying out an overcoat is also performed by calcinating.

[0004] High-tension-proof pulse characteristics (ESD property) are in one of the important properties of a thick film resistor. Usually, an ESD property worsens by the resistance more than 10k Ω /**. The reason is as follows. Although the conductivity of a thick film resistor is materialized by the thin film of the glass between the conductive material formed into glass, if high tension is impressed to a thick film resistor, a detailed electric conduction path will be destroyed and resistance will change. Since the loadings of conductive material decrease and the flow by the thin film of glass becomes dominant so that it becomes high resistance, the above-mentioned phenomenon becomes easy to occur. For solution of this phenomenon, the following cures were taken conventionally.

[0005] (1) Use the powder of Bi₂Ru₂O₇ with large resistivity, and Pb₂Ru₂O₆, and make [many] combination of conductive material. However, glass uses the thing containing Pb for decomposition prevention.

(2) Make the thin film form between electric conduction particles during baking using the low melting glass of Pb content.

[0006] (3) Use that of a fine potato for glass powder and an electric conduction particle dramatically, and make [many] an electric conduction path. (Refer to JP,8-250829,A)

However, since (1) and (2) contained Pb which is harmful matter in the raw material, its distributed approach was difficult for (3) preferably.

[0007]

[Problem(s) to be Solved by the Invention] Then, the ESD property of this invention is good and it aims at offering the thick-film resistive paste which moreover does not contain harmful matter, such as Pb, Cd, and nickel, and obtaining the ceramic circuit board of the outstanding engine performance.

[0008]

[Means for Solving the Problem] In the thick-film resistive paste which makes the mixture which comes to mix the raw material powder with which this invention consists of glass powder and powder of conductive material with an organic vehicle come to add an organic vehicle, a solvent,

and a dispersant further When the minor-axis particle size of this raw material powder makes B % the volume rate of as opposed to this raw material powder of Am²/g and this organic vehicle for average specific surface area, by 5 micrometers or less, it is thick-film resistive paste characterized by using the mixture which has the relation of $5.5 A \leq B \leq 10.0A$.

[0009] In the above, if it is difficult for the amount of vehicles to have too little B under at 5.5A, and to make fine particles adhere to a roller and it exceeds 10.0A, since there are many amounts of vehicles, distribution of glass powder and the powder of conductive material cannot be performed, but the effectiveness over an EDS property will seldom be demonstrated. In addition, when 10 pa-s - 300 pa-s is suitable for the viscosity of an organic vehicle and is smaller than 10 pa-s, it does not have adhesion, and it becomes difficult to make fine particles adhere to a roller. Moreover, if 300 Pa-s is exceeded, since fine particles cannot be uniformly soaked in a vehicle, it will be necessary to dilute with volatile solvents (for example, toluene, ethanol, etc.).

[0010] CaO-aluminum₂O₃-SiO₂-B₂O₃, Na₂O-SiO₂-B₂O₃, and the thing that does not contain Pb, Cd, and nickel with these mixed glass further are used for glass powder among powder ingredients. RuO₂ is used as conductive material. As an organic vehicle, ethyl cellulose, a terpeneol, butyral resin, a terpeneol, etc. are used.

[0011] In the process which this invention passes [process] a clearance 5 micrometers or less for the mixture which consists of a powder ingredient and an organic vehicle compulsorily again, and makes an organic vehicle distribute a raw material powder ingredient When the volume rate of Am²/g and an organic vehicle is made into B % for the average specific surface area of raw material powder, it is the manufacture approach of the thick-film resistive paste characterized by consisting of mixture which has the relation of $5.5 A \leq B \leq 10.0A$, and nothing and the process which adds and kneads an organic vehicle, a solvent, and a dispersant further. First, distribution of glass and conductive material can be made into homogeneity by passing a clearance 5 micrometers or less for the mixture which has the relation of Above A and B compulsorily.

[0012] A clearance 5 micrometers or less is obtained by arranging two parallel rollers at intervals of 5 micrometers. By making this clearance pass an ingredient compulsorily, a path crushes or crushes the powder exceeding 5 micrometers, and considers as the magnitude of 5 micrometers or less. In this case, although it does not interfere even if a powdered major axis exceeds 5 micrometers, 2 double less or equal of a minor axis is suitable. Since the force will not join powder if a clearance exceeds 5 micrometers, it cannot fully distribute. In order to make the paste which can be printed the ingredient distributed through the clearance, it adds and kneads an organic vehicle and a solvent, and uses them as thick-film resistive paste as suitable viscosity.

[0013]

[Embodiment of the Invention] Hereafter, the example of a comparison is explained to the example list of this invention. Three sorts of following things were prepared as glass powder.

[0014]

[A table 1]

| | CaO | Al ₂ O ₃ | SiO ₂ | B ₂ O ₃ | Na ₂ O | K ₂ O | その他 |
|---|------|--------------------------------|------------------|-------------------------------|-------------------|------------------|-----|
| a | 25.0 | 4.2 | 54.0 | 16.1 | — | — | 0.7 |
| b | 33.0 | 4.2 | 44.9 | 16.2 | — | — | 1.7 |
| c | 4.2 | 2.5 | 66.3 | 21.7 | 3.0 | 0.9 | 1.4 |

[0015] Moreover, two sorts of following things were prepared as a vehicle.

X -- Ethyl cellulose, the Tell Young Pioneers Y -- RuO₂ was used as butyral resin and Tell Young Pioneers + butyl carbitol acetate conductive material.

[0016] After creating mixture to homogeneity with the configuration which shows these ingredients in a table 2, in order to consider as the paste which can be printed, an organic vehicle, an additional solvent, and an additional dispersant (HOMOG E Norian L-95 {trade name:} by Kao Corp.) were added and kneaded, and thick-film resistive paste was created. This was formed on the low-temperature baking ceramic substrate, and the pattern printing of the resistance polar zone, and after calcinating, the thick film resistor was formed on the ceramic substrate. A multiplier is collectively shown in a table 2 at the sheet resistance (kohms) of the obtained resistor, 1.5kV, ESD in five pulses,

and a list.

[0017]

[A table 2]

表 2

| No. | | RuO ₂ BET (m ² /g) | RuO ₂ 配合 (%) | ガラス 種類 | ガラス BET (m ² /g) | ガラス 配合 (%) | 平均 BET (m ² /g) | ビニル 種類 | ビニル配合 (質量%) | ビニル粘度 (Pa·s) | ローラ間隔 (μm) | シート抵抗 (kΩ) | ESD | 係数 |
|-----|----|--|-------------------------------|-----------|-----------------------------------|------------------|----------------------------------|-----------|----------------|-----------------|---------------|---------------|------|-----|
| 実施例 | 1 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 3 | 97 | -0.5 | 8 |
| | 2 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 60 | 100 | 3 | 120 | -0.3 | 6 |
| | 3 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 55 | 100 | 3 | 130 | -0.2 | 5.5 |
| | 4 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 100 | 100 | 3 | 82 | -0.9 | 10 |
| | 5 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 0.5 | 123 | -0.2 | 8 |
| | 6 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 5 | 84 | -0.8 | 8 |
| | 7 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 300 | 3 | 117 | -0.3 | 8 |
| | 8 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 10 | 3 | 88 | -0.7 | 8 |
| | 9 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 82 | 100 | 3 | 14 | -0.3 | 8 |
| | 10 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 82 | 100 | 0.5 | 16 | -0.1 | 8 |
| | 11 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 82 | 100 | 5 | 12 | -0.5 | 8 |
| | 12 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 57 | 100 | 0.5 | 16 | -0.2 | 5.5 |
| | 13 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 103 | 100 | 0.5 | 13 | -0.8 | 10 |

[0018]

[A table 3]

表 2 つづき

| No. | | RuO ₂ BET (m ² /g) | RuO ₂ 配合 (%) | ガラス 種類 | ガラス BET (m ² /g) | ガラス配 合 (%) | 平均 BET (m ² /g) | ビニル 種類 | ビニル配合 (質量%) | ビニル粘度 (Pa・s) | ローラ間隔 (μm) | シート抵抗 (kΩ) | ESD | 係数 |
|-----|----|--|-------------------------------|-----------|-----------------------------------|------------------|----------------------------------|-----------|----------------|-----------------|---------------|---------------|------|-----|
| 実施例 | 14 | 15 | 30 | a | 9.1 | 70 | 10.9 | X | 109 | 100 | 5 | 1.5 | -0.1 | 10 |
| | 15 | 15 | 35 | a | 9.1 | 70 | 11.6 | X | 116 | 100 | 5 | 0.55 | -0.1 | 10 |
| | 16 | 12 | 15 | a | 7.5 | 85 | 8.2 | X | 65 | 100 | 3 | 66 | -0.7 | 8 |
| | 17 | 37 | 15 | a | 14 | 85 | 17.5 | X | 140 | 100 | 3 | 186 | -0.2 | 8 |
| | 18 | 15 | 15 | b | 8.3 | 85 | 9.3 | X | 74 | 100 | 3 | 104 | -0.3 | 8 |
| | 19 | 15 | 15 | b | 8.3 | 85 | 9.3 | Y | 74 | 122 | 3 | 112 | -0.3 | 8 |
| | 20 | 15 | 15 | c | 8.8 | 85 | 9.7 | Y | 78 | 140 | 2 | 129 | -0.2 | 8 |
| 比較例 | 21 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 120 | 100 | 3 | 52 | -1.2 | 12 |
| | 22 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 7 | 42 | -1.8 | 8 |
| | 23 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 45 | 100 | 3 | 不可 | — | 4.5 |

[0019] No.1-20 which are the example of this invention excel [property / EDS] in 1.0% or less, a convention of the relational expression in this invention is not satisfied, EDS is over 1.0%, and the examples 21-22 of a comparison are getting worse as shown in the above-mentioned table.

Moreover, the example 23 of a comparison does not satisfy a convention of the relational expression in this invention, either, but paste production is difficult for it.

[0020]

[Effect of the Invention] According to this invention, the thick-film resistive paste which was

excellent in the ESD property can be offered, and the ceramic circuit board of the outstanding engine performance can be obtained. This paste can be offered without including harmful matter, such as Pd, Cd, and nickel, in raw material powder, and when keeping the operating environment of a product good, it is effective.

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SOLUTION: A film resistance paste is prepared by adding an organic vehicle, a solvent, and a dispersant to a mixture prepared by mixing raw material powder composed of glass powder and conductive material powder with the organic vehicle. The mixture is prepared for satisfying the relation, $5.5A \leq B \leq 10.0A$ (where A represents the mean specific surface area (Am^2/g) of the raw material powder, when the minor-axis diameter of the powder is less than or equal to $5\mu\text{m}$ and the volumetric ratio (%) of the vehicle to the raw material powder is B). At the manufacturing of the paste, the raw material powder is dispersed in the organic vehicle by forcibly passing the raw material mixture through a clearances of less than or equal to $5\mu\text{m}$ in width.

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(54) 【発明の名称】 厚膜抵抗ペーストおよびその製造方法

(57) 【要約】

【課題】 EDS特性が良く、しかもPd, Cd, Niなどの有害物質を含まない厚膜抵抗ペーストを提供し、優れた性能のセラミック回路基板を得ることを目的とする。

【解決手段】 ガラス粉末と導電物質の粉末からなる原料粉末を有機ビヒクルで混合してなる混合物にさらに有機ビヒクル、溶剤及び分散剤を添加させてなる厚膜抵抗ペーストにおいて、該原料粉末の短軸粒径が $5\mu\text{m}$ 以下で平均比表面積を $\text{A m}^2/\text{g}$ 、該有機ビヒクルの該原料粉末に対する体積割合をB%としたとき、 $5.5\text{A} \leq \text{B} \leq 10.0\text{A}$ の関係の有する混合物を用いたことを特徴とする厚膜抵抗ペーストと、原料混合物を $5\mu\text{m}$ 以下の隙間を強制的に通過させて粉末材料を有機ビヒクルに分散させる同ペーストの製造方法である。

【特許請求の範囲】

【請求項 1】 ガラス粉末と導電物質の粉末からなる原料粉末を有機ビヒクルで混合してなる混合物にさらに有機ビヒクル、溶剤及び分散剤を添加させてなる厚膜抵抗ペーストにおいて、該原料粉末の短軸粒径が $5\mu\text{m}$ 以下で平均比表面積を Am^2/g 、該有機ビヒクルの該原料粉末に対する体積割合を $\text{B}\%$ としたとき、 $5.5\text{A} \leq \text{B} \leq 10.0\text{A}$ の関係を有する混合物を用いたことを特徴とする厚膜抵抗ペースト。

【請求項 2】 上記原料粉末材料が Pb 、 Cd 、 Ni を含まないものである請求項 1 記載の厚膜抵抗ペースト。

【請求項 3】 上記導電物質が RuO_2 である請求項 1 記載の厚膜抵抗ペースト。

【請求項 4】 粉末材料と有機ビヒクルからなる混合物を $5\mu\text{m}$ 以下の隙間を強制的に通過させて、原料粉末材料を有機ビヒクルに分散させる工程において、原料粉末の平均比表面積を Am^2/g 、有機ビヒクルの体積割合を $\text{B}\%$ としたとき、 $5.5\text{A} \leq \text{B} \leq 10.0\text{A}$ の関係を有する混合物となし、さらに有機ビヒクル、溶剤及び分散剤を添加し混練する工程からなることを特徴とする厚膜抵抗ペーストの製造方法。

【請求項 5】 上記原料粉末材料が Pb 、 Cd 、 Ni を含まないものである請求項 4 記載の厚膜抵抗ペーストの製造方法。

【請求項 6】 上記導電物質が RuO_2 である請求項 4 記載の厚膜抵抗ペーストの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、外部抵抗体を有するセラミック回路基板用の厚膜抵抗ペーストおよびその製造方法に関する。

【0002】

【従来の技術】 集積回路に使用されるセラミック回路基板において、多層回路基板の層間に設けられる内蔵抵抗体の他に、セラミック基板の表面に導体パターンや外部抵抗体などからなる回路を形成し、セラミック回路基板の高機能化、低コスト化に貢献している。

【0003】 セラミック基板表面に厚膜抵抗体を形成する場合、ガラス粉末に導電物質を加え有機ビヒクルでペースト状にしたものを基板表面に印刷し、焼結して抵抗体とする。このとき、抵抗体の保護や耐候性の向上を目的として、抵抗体をガラス系材料で覆うように印刷し、焼成することによってオーバーコートすることも行われている。

【0004】 厚膜抵抗体の重要な特性の一つに耐高電圧パルス特性（ESD 特性）がある。通常 $10\text{k}\Omega/\square$ 以上の抵抗で EDS 特性が悪くなる。その理由は以下の通りである。厚膜抵抗体の導電性はガラス中に形成される導電物質と導電物質間のガラスの薄い膜で成立しているが、厚膜抵抗体に高電圧が印加されると微細な導電経路

は破壊され抵抗値が変化する。高抵抗になる程、導電物質の配合量が減少し、ガラスの薄い膜による導通が支配的になるため、上記の現象は起きやすくなる。かかる現象の解決のために、従来は以下のような対策が講じられていた。

【0005】 (1) 抵抗率の大きい $\text{Bi}_2\text{Ru}_2\text{O}_7$ 、 $\text{Pb}_2\text{Ru}_2\text{O}_6$ の粉末を使用し、導電物質の配合を多くする。ただし分解防止のためガラスは Pb を含むものを使用する。

(2) Pb 含有の低融点ガラスを用い、焼成中に導電粒子間に薄い膜を形成させる。

【0006】 (3) ガラス粉末、導電粒子を非常に細かいものを使用し、導電経路を多くする。（特開平 8-250829 号公報参照）

しかし、(1)、(2) は原材料中に有害物質である Pb を含むので好ましくなく、(3) は分散方法が難しかった。

【0007】

【発明が解決しようとする課題】 そこで本発明は、ESD 特性が良く、しかも Pb 、 Cd 、 Ni などの有害物質を含まない厚膜抵抗ペーストを提供し、優れた性能のセラミック回路基板を得ることを目的とする。

【0008】

【課題を解決するための手段】 本発明は、ガラス粉末と導電物質の粉末からなる原料粉末を有機ビヒクルで混合してなる混合物にさらに有機ビヒクル、溶剤及び分散剤を添加させてなる厚膜抵抗ペーストにおいて、該原料粉末の短軸粒径が $5\mu\text{m}$ 以下で平均比表面積を Am^2/g 、該有機ビヒクルの該原料粉末に対する体積割合を $\text{B}\%$ としたとき、 $5.5\text{A} \leq \text{B} \leq 10.0\text{A}$ の関係を有する混合物を用いたことを特徴とする厚膜抵抗ペーストである。

【0009】 上記において、 B が 5.5A 未満ではビヒクル量が少なすぎてローラに粉体を付着させることが困難であり、 10.0A を越えるとビヒクル量が多いため、ガラス粉末と導電物質の粉末の分散ができず、EDS 特性に対する効果があり発揮されない。なお、有機ビヒクルの粘度は $10\text{Pa}\cdot\text{s} \sim 300\text{Pa}\cdot\text{s}$ が適当で $10\text{Pa}\cdot\text{s}$ より小さいと粘着力がなく、ローラに粉体を付着させることが困難となる。又、 $300\text{Pa}\cdot\text{s}$ を越えると、粉体をビヒクルで一様に濡らすことができないため、揮発性の溶剤（例えばトルエン、エタノール等）で希釈する必要が生じる。

【0010】 粉末材料のうち、ガラス粉末は、 $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3$ 、 $\text{Na}_2\text{O}-\text{SiO}_2-\text{B}_2\text{O}_3$ 、さらにはこれらの混合ガラスで Pb 、 Cd 、 Ni を含まないものを用いる。導電物質としては RuO_2 を用いる。有機ビヒクルとしては、エチルセルロースとテルピネオール、ブチラル樹脂とテルピネオールなどが用いられる。

【0011】本発明は又、粉末材料と有機ビヒクルからなる混合物を $5\mu\text{m}$ 以下の隙間を強制的に通過させて、原料粉末材料を有機ビヒクルに分散させる工程において、原料粉末の平均比表面積を $\text{A m}^2/\text{g}$ 、有機ビヒクルの体積割合を $\text{B}\%$ としたとき、 $5.5\text{A} \leq \text{B} \leq 10.0\text{A}$ の関係を有する混合物となし、さらに有機ビヒクル、溶剤及び分散剤を添加し混練する工程からなることを特徴とする厚膜抵抗ペーストの製造方法である。まず、上記 A と B の関係を有する混合物を $5\mu\text{m}$ 以下の隙間を強制的に通過させることによって、ガラスと導電物質の分散を均一にすることができる。

【0012】 $5\mu\text{m}$ 以下の隙間は例えば2本の平行ローラを $5\mu\text{m}$ 間隔で配置することによって得られる。材料をこの隙間に強制的に通過させることによって、径が 5

μm を越える粉末を破碎あるいは押しつぶし、 $5\mu\text{m}$ 以下の大きさとする。この場合、粉末の長軸は $5\mu\text{m}$ を越えてもさしつかえないが、短軸の2倍以下が適当である。隙間が $5\mu\text{m}$ を越えると粉末に力が加わらないため、十分に分散することができない。隙間を通して分散した材料は、印刷可能なペーストにするため、有機ビヒクルおよび溶剤を追加して混練し、適当な粘度として厚膜抵抗ペーストとする。

【0013】

【発明の実施の形態】以下、本発明の実施例並びに比較例について説明する。ガラス粉末として下記の3種のものを用意した。

【0014】

【表1】

| | CaO | Al ₂ O ₃ | SiO ₂ | B ₂ O ₃ | Na ₂ O | K ₂ O | その他 |
|---|------|--------------------------------|------------------|-------------------------------|-------------------|------------------|-----|
| a | 25.0 | 4.2 | 54.0 | 16.1 | — | — | 0.7 |
| b | 33.0 | 4.2 | 44.9 | 16.2 | — | — | 1.7 |
| c | 4.2 | 2.5 | 66.3 | 21.7 | 3.0 | 0.9 | 1.4 |

【0015】又、ビヒクルとしては下記の2種のものを用意した。

X…エチルセルロース、テルピオネール

Y…ブチラル樹脂、テルピオネール+ブチルカルビトールアセテート

導電物質としてはRuO₂を用いた。

【0016】これらの材料を表2に示す構成で混合物を均一に作成した後、印刷可能なペーストとするために追加の有機ビヒクル、溶剤及び分散剤（ホモゲノールレー

95〔商品名：花王株式会社製〕を追加して混練し、厚膜抵抗ペーストを作成した。これを低温焼成セラミックス基板上に抵抗電極部のパターン印刷、焼成した後、セラミック基板上に厚膜抵抗体を形成した。得られた抵抗体のシート抵抗（ $\text{k}\Omega$ ）、 1.5kV 、5パルスにおけるESD、並びに係数を表2に併せて示す。

【0017】

【表2】

表 2

| No. | | RuO ₂ BET (m ² /g) | RuO ₂ 配合 (%) | ガラス 種類 | ガラス BET (m ² /g) | ガラス配 合 (%) | 平均 BET (m ² /g) | ビヒクル 種類 | ビヒクル配合 (重量%) | ビヒクル粘度 (p・s) | ローラ間隙 (μm) | シート抵抗 (kΩ) | ESD | 係数 |
|-------------|----|--|-------------------------------|-----------|-----------------------------------|------------------|----------------------------------|------------|-----------------|-----------------|---------------|---------------|------|-----|
| 実 施 例 | 1 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 3 | 97 | -0.5 | 8 |
| | 2 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 60 | 100 | 3 | 120 | -0.3 | 6 |
| | 3 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 55 | 100 | 3 | 130 | -0.2 | 5.5 |
| | 4 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 100 | 100 | 3 | 82 | -0.9 | 10 |
| | 5 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 0.5 | 123 | -0.2 | 8 |
| | 6 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 5 | 84 | -0.8 | 8 |
| | 7 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 300 | 3 | 117 | -0.3 | 8 |
| | 8 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 10 | 3 | 88 | -0.7 | 8 |
| | 9 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 82 | 100 | 3 | 14 | -0.3 | 8 |
| | 10 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 82 | 100 | 0.5 | 16 | -0.1 | 8 |
| | 11 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 82 | 100 | 5 | 12 | -0.5 | 8 |
| | 12 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 57 | 100 | 0.5 | 16 | -0.2 | 5.5 |
| | 13 | 15 | 20 | a | 9.1 | 80 | 10.3 | X | 103 | 100 | 0.5 | 13 | -0.8 | 10 |

【0018】

【表3】

表2つづき

| No. | | RuO ₂ BET (m ² /g) | RuO ₂ 配合 (%) | ガラス 種類 | ガラス BET (m ² /g) | ガラス配 合 (%) | 平均 BET (m ² /g) | ビニル 樹脂 | ビニル配合 (重量%) | ビニル樹脂 (p.p.s) | ローテ樹脂 (μm) | シート抵抗 (kΩ) | ESD | 係数 |
|-----|----|--|-------------------------------|-----------|-----------------------------------|------------------|----------------------------------|-----------|----------------|------------------|---------------|---------------|------|-----|
| 実施例 | 14 | 15 | 30 | a | 9.1 | 70 | 10.9 | X | 109 | 100 | 5 | 1.5 | -0.1 | 10 |
| | 15 | 15 | 35 | a | 9.1 | 70 | 11.6 | X | 116 | 100 | 5 | 0.55 | -0.1 | 10 |
| | 16 | 12 | 15 | a | 7.5 | 85 | 8.2 | X | 65 | 100 | 3 | 66 | -0.7 | 8 |
| | 17 | 37 | 15 | a | 14 | 85 | 17.5 | X | 140 | 100 | 3 | 186 | -0.2 | 8 |
| | 18 | 15 | 15 | b | 8.3 | 85 | 9.3 | X | 74 | 100 | 3 | 104 | -0.3 | 8 |
| | 19 | 15 | 15 | b | 8.3 | 85 | 9.3 | Y | 74 | 122 | 3 | 112 | -0.3 | 8 |
| | 20 | 15 | 15 | c | 8.8 | 85 | 9.7 | Y | 78 | 140 | 2 | 129 | -0.2 | 8 |
| 比較例 | 21 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 120 | 100 | 3 | 52 | -1.2 | 12 |
| | 22 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 80 | 100 | 7 | 42 | -1.8 | 8 |
| | 23 | 15 | 15 | a | 9.1 | 85 | 10.0 | X | 45 | 100 | 3 | 不可 | — | 4.5 |

【0019】上記表に示すとおり、本発明の実施例であるNo. 1～20はESD特性が1.0%以下で優れたものであり、比較例21～22は本発明における関係式の規定を満足しないもので、ESDが1.0%を越えており悪くなっている。又、比較例23も本発明における関係式の規定を満足しておらず、ペースト作製が困難である。

【0020】

【発明の効果】本発明によればESD特性の優れた厚膜抵抗ペーストを提供することができ、優れた性能のセラミック回路基板を得ることができる。このペーストは原料粉末にPd, Cd, Ni等の有害物質を含むことなく提供でき、製品の使用環境を良好に保つ上で効果がある。

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